



## Liquid Crystal of Ethyl and Propyl Aromatic Aldehyde with Azo Core and Photosensitivity in Mesophase

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Received: 23 June 2014;

Accepted: 11 September 2014;

Published online: 20 February 2015;

AJC-16913

Eight new stable rod-like aromatic aldehyde liquid crystalline molecules with azo bridge have been prepared, in which single or double six-membered carbon ring carboxylic acid mesogenic cores with shorter alkyl chain of ethyl, *n*-propyl were condensed with hydroxyl azo benzaldehyde. These compounds have been characterized by their spectral data, DSC and HS-POM. These molecules were expected to exhibit liquid crystal phase so that the influence of UV-light on their textures of mesophase could be detected. The results showed that all these target compounds have the temperature range of mesophase between 101 and 145 °C. After irradiating under UV-light, they exhibited photo-sensitivity not only in methanol but also in mesophase.

**Keywords:** Liquid crystals, Photosensitivity, Azo compound, Aromatic aldehyde.

### INTRODUCTION

Functionalizing molecular structures to make them response to outer stimuli such as magnetism, thermal and light is an important way to innovate new materials<sup>1</sup>. Great interest is recently attracted to molecules that have two or more forms so that the interconversion between them can triggered by external stimulus<sup>2-4</sup>. Some literature studied the effect of UV-light on solid state of substance<sup>5</sup>, but little report involved influence of UV-light on mesophase of micromolecules.

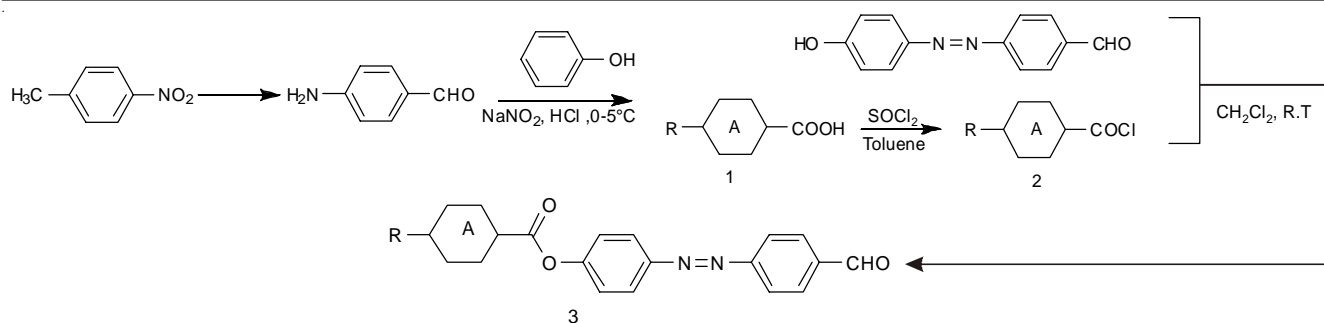
It's well known that the molecular architecture is an important factor for a molecule to exhibit its mesophase. Azo liquid crystals reported in literature usually made up of terminal longer alkoxy chain<sup>6,7</sup>, which is easy to be synthesized by converting hydroxy group into different ethers in one-step reaction. Being more stable than alkoxy group, terminal alkyl chains usually made by multi-step reactions is seldom used in designing molecules of liquid crystals. Some publication reported study on the effect of a polar end group on the mesomorphic property<sup>8</sup>, but few of them involved aldehyde as an end group. Previous papers<sup>9</sup> have designed some series liquid crystals with a polar end group of CHO, which exhibit an mesophase even with shorter alkyl chain ( $n \geq 2$ ). These compounds have thermostability and wider temperature range of mesophase than other common functional groups, for example alkyls, alkoxy groups or cyanogroup. In addition, aromatic aldehyde is easier to convert into other groups, such as aromatic acid<sup>10</sup>, Schiff base<sup>11</sup> or other functional molecules<sup>12</sup>. We have

synthesized 8 rod-like liquid crystalline molecules consisted of shorter terminal alkyl chain of C2 and C3, aldehyde and azo bridge bonding, by changing the terminal single six-membered carbon ring from cyclohexyl to phenyl or double six-membered carbon rings from cyclohexyl benzene to biphenyl in order to obtain the effect of these variations on their liquid crystalline property in the mean time to study their photo-sensitivity when *cis-trans* isomerization takes place and azo molecules change their shapes. (their structure and synthesis pathway is shown as **Scheme-I**).

### EXPERIMENTAL

All initial intermediates used in the synthesis were prepared in our laboratory with purity higher than 99 % and characterized by IR, GC-MS and <sup>1</sup>H NMR methods. Other reagents were obtained from commercial sources and used without further purification. 4'-Hydroxybenzene-azo-4-benzaldehyde were synthesised according to literature<sup>13</sup>.

The purities of compounds were detected by LC-10A (Shimadzu) instrument with methanol as eluent and flowing rate was 1 mL/min. Elemental analyses were conducted by PE-2400 analyzer (Perkin Elmer). The irradiation of samples was carried out by hand-held UV-lamp ZF-7A (Shanghai Jiapeng Technology Co. Ltd.). UV-spectra were determined by Agilent 8453 Spectrometer (Agilent Technologies). IR (KBr) spectra were recorded on a Vertex 70 spectrophotometer (BRUKER). Mass data were recorded on a GCMS-QP2010



a: R=ethyl, A=*trans*-cyclohexyl; b: R=*n*-propyl, A=*trans*-cyclohexyl c: R=ethyl, A=phenyl; d: R=*n*-propyl, A=phenyl  
e: R=ethyl, A=*trans*-cyclohexyl phenyl; f: R=*n*-propyl, A=*trans*-cyclohexyl phenyl g: R=ethyl, A=biphenyl; h: R=*n*-propyl, A=biphenyl

Scheme-I: Synthesis process of resulting compounds

(Shimadzu) and IE was 70 ev.  $^1\text{H}$  NMR were obtained on a BRUKER AV 500 spectrometer (500 MHz, solvent  $\text{CDCl}_3$ ). The DSC experiments were carried out on MDSC Q100 instrument (TA) and the determination conditions were: the sample mass less than 5 mg; heating rate,  $1^\circ\text{C}/\text{min}$  and samples were protected by nitrogen. The TGA experiments were carried out on Q500 instrument (TA). All images of textures were taken on a LV100POL Polarizing Optical Microscopy (Nikon) with LTS E350 thermalplate (Linkam) and heating rate  $1^\circ\text{C}/\text{min}$ .

**Synthesis of compound 2:** Compound **2a** was prepared by heating and stirring a mixture of compound *p*-ethyl benzoic acid (**1a**) (1.16 g, 5 mmol) and  $\text{SOCl}_2$  (0.59 g, 5 mmol) and several drops of DMF in toluene (30 mL) at ambient temperature for 5 h, then the solvent was removed under reduced pressure. A brown liquid (**2a**) was obtained and used to next step without further purifying.

**Synthesis of compounds 3:** Compound **3a** was obtained by dissolving compound *p*-ethyl benzoyl chloride (**1a**) (0.78 g, 5 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) and dropped the mixture into a solution of 4'-hydroxy-benzene-azo-4-benzaldehyde (1.13 g, 5 mmol) and triethylamide (0.9 mL, 5 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) and stirred at ambient temperature for 12 h, then the reacting solvent was removed under vacuum condition. Some orange solid was obtained, washing with 5 % (mass fraction) NaOH and water. The residue was dried and recrystallized with THF, then an orange powder (**3a**, 0.84 g) was obtained in yield of 84 % (two steps). The compounds **3b-3h** were also prepared by the same way and their yields were 84, 83, 83, 85, 86, 83 and 87 %, respectively.

**4-[4-(4-Ethylcyclohexylacyloxy)phenyldiazenyl]benzaldehyde (3a):** Relative molecular mass: 364.44, the mass fraction detected by LC is 98.8 %, orange powder, m.p.  $85-86^\circ\text{C}$ ; Anal. Calcd. for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3$ : C 72.50, H 6.64, N 7.69; found: C 72.34, H 6.69, N 7.62; IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2959, 2930 (s, C-H), 2852, 2744 (s, H of aldehyde), 2361, 2343, 1749 (vs, C=O), 1694 (vs, C=O), 1654, 1637 (m, N=N), 1559, 1495, 1458 (m, ArH), 1448, 1378, 1318, 1297, 1255, 1202, 1156, 1124, 1099, 1007 (vs, C-O-C), 995, 902, 855 (s, *trans*-H-N=N-R), 841, 817 (w, 1,4-Ar), 760, 725, 662 (w,  $(\text{CH}_2)_n$ ); MS (70 ev)  $m/z$  (%): 364 ( $\text{M}^+$ , 3.79), 360(0.26), 351 (0.03), 269 (0.08), 257 (0.30), 242 (33.81), 224 (1.09), 215 (0.25), 197 (0.22), 185 (0.26), 168 (0.17), 157 (0.19), 147 (1.60), 139 (12.54), 121 (31.37), 111 (55.06), 93 (8.83), 91 (2.09), 84 (0.11), 69 (100), 65 (21.13), 61 (0.30), 57 (2.34), 55 (19.26),

51 (1.35), 41 (11.53);  $^1\text{H}$  NMR: 0.912 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 0.979-1.039 (m, 2H,  $\text{CH}_2$ ), 1.212-2.528 (m, 10 H, proton of cyclohexane), 7.249(m, 4H), 8.000, 8.028 (d,  $J = 8.4$  Hz, 8.6 Hz, 2H of each), 10.108 (s, 1H, CHO).

**4-[4-(4-*n*-Propylcyclohexylacyloxy)phenyldiazenyl]benzaldehyde (3b):** Relative molecular mass: 378.46, the mass fraction detected by LC is 98.7 %, orange powder, m.p.  $99-100^\circ\text{C}$ ; Anal. Calcd. for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_3$ : C 72.99, H 6.92 N 7.40; found C 72.87, H 7.01, N 7.35 IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2954, 2929 (s, C-H), 2858, 2747 (s, H of aldehyde), 2679, 2361, 2343, 1748 (vs, C=O), 1698 (vs, C=O), 1671, 1648 (m, N=N), 1599, 1559, 1541, 1508, 1496, 1457 (m, ArH), 1376, 1315, 1202, 1164, 1123 (vs, C-O-C), 977, 869, 814 (w, 1, 4-Ar), 797,762, 727, 669 (w,  $(\text{CH}_2)_n$ ), 553; MS (70 ev)  $m/z$  (%): 378 ( $\text{M}^+$ , 9.61), 364 (0.14), 350 (0.08), 335 (0.02), 313 (0.02), 273 (0.07), 261 (0.05), 245 (0.21), 229 (0.11), 226 (50.73), 212 (0.79), 197 (0.08), 181 (0.01), 161 (0.17), 153 (11.91), 152 (3.13), 133 (0.70), 125 (61.48), 121 (28.24), 120 (0.73), 105 (3.30), 93 (12.91), 92 (0.81), 86 (0.85), 83 (45.90), 77 (1.35), 69 (100), 67 (5.16), 57 (21.68), 51 (0.28), 41 (4.35), 29 (0.44);  $^1\text{H}$  NMR: 0.902 (t, 3H,  $J = 1.6$  Hz,  $\text{CH}_3$ ), 0.954-1.049 (m, 2H,  $\text{CH}_2$ ), 1.182-1.236 (m, 2H,  $\text{CH}_2$ ), 1.525-2.555 (m, 10H, the proton of cyclohexane), 7.256 (d,  $J = 8.5$  Hz, 2H of each), 7.986-8.033 (m, 6H), 11.105 (s, 1H, CHO).

**4-[4-(4-Ethylbenzoyloxy)phenyldiazenyl]benzaldehyde (3c):** Relative molecular mass: 358.39, mass fraction detected by LC is 98.7 %, orange powder, m.p.  $129-130^\circ\text{C}$ ; Anal. Calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3$ : C 73.73, H 5.06, N 7.82; found C 73.69, H 5.11, N 7.76; IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3067, 2969, 2931, 2875 (s, C-H), 2815, 2726 (H of aldehyde), 1731 (vs, C=O), 1698 (vs, C=O), 1609, 1599, 1507, 1496, 1465, 1416, 1309, 1271, 1202, 1140, 1078, 1011 (vs, C-O-C), 929, 886, 848, 760, 725, 696, 661; MS (70 ev)  $m/z$  (%): 358 ( $\text{M}^+$ , 1.28), 257 (0.37), 241 (0.06), 226 (0.37), 211 (0.02), 167 (0.10), 150 (0.04), 141 (0.17), 132 (0.94), 133 (100), 121 (1.58), 105 (7.29), 93 (2.15), 79 (2.77), 65 (0.98), 57 (0.03), 51 (0.11), 44 (0.14), 39 (0.12), 32 (0.12);  $^1\text{H}$  NMR: 1.300 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.765 (q, 2H,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 7.364, 7.414, 8.145 (d,  $J = 8.0$  Hz, 8.4 Hz, 8.0 Hz, 2H of each), 8.069-8.086 (m, 6H, H of benzene ring), 10.114 (s, 1H, CHO).

**4-[4-(4-*n*-Propylbenzoyloxy)phenyldiazenyl]benzaldehyde (3d):** Relative molecular mass: 372.42, mass fraction detected by LC is 98.8 %, orange powder, m.p.  $123-124^\circ\text{C}$ ; Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_3$ : C 74.18, H 5.41, N 7.52; found

C 74.03, H 5.52, N 7.46; IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3065, 2960, 2930 (s, C-H), 2872, 2814, 2723 (H of aldehyde), 2361, 2342, 1732 (vs, C=O), 1698 (vs, C=O), 1653, 1610, 1590, 1559, 1541, 1496, 1457 (m, ArH), 1417, 1310, 1270, 1196, 1179, 1143, 1100, 1079, 1011 (vs, C-O-C), 885, 846 (w, 1, 4-Ar) 756, 696 (w,  $(\text{CH}_2)_n$ ); MS (70 ev)  $m/z$  (%): 372 ( $\text{M}^+$ , 1.50), 317 (0.02), 255 (0.05), 239 (0.02), 225 (0.22), 209 (1.88), 181 (0.23), 165 (0.07), 149 (0.74), 147 (100), 131 (0.60), 121 (0.67), 119 (5.07), 105 (0.71), 93 (0.78), 91 (7.17), 77 (0.56), 65 (0.39), 51 (0.07), 41 (0.53), 32 (0.31);  $^1\text{H NMR}$ : 0.975 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 1.676-1.732 (m, 2H,  $\text{CH}_2$ ), 2.699 (t, 2H,  $J = 7.6$  Hz,  $\text{CH}_2$ ), 7.340, 7.411, 8.048 (d,  $J = 8.0$  Hz, 8.4 Hz, 8.0 Hz, 2H of each), 8.138-8.156 (m, 6H), 10.111 (s, 1H, CHO).

**4-[4-(4-(4-Ethylcyclohexyl)benzoyloxy)phenyldiazenyl]benzaldehyde (3e)**: Relative molecular mass: 440.53; the mass fraction detected by LC is 99.1 %, orange powder, m.p. 128-129 °C; Anal. Calcd. for  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_3$ : C 76.34, H 6.41, N 6.36; found: C 76.23, H 6.55, N 6.23; IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 2957, 2917 (s, C-H), 2849, 2729 (s, H of aldehyde), 2361, 2342, 1741 (vs, C=O), 1703 (vs, C=O), 1648, 1636 (N=N), 1598, 1559, 1541, 1508, 1495, 1458 (m, ArH), 1418, 1375, 1308, 1272, 1223, 1198, 1178, 1139, 1099, 1063, 1009 (vs, C-O-C), 985, 924, 884 (s, *trans*-R-N=N-R), 837, 819 (w, 1,4-Ar), 775(w,  $(\text{CH}_2)_n$ ), 761, 699, 684; MS (70 ev)  $m/z$  (%): 440 ( $\text{M}^+$ , 1.60), 426 (0.14), 364 (0.05), 323 (0.11), 293 (0.02), 243 (0.40), 217(1.55), 215(100), 199(0.05), 187(0.16), 171(0.05), 157 (0.14), 145 (0.30), 131 (1.14), 121 (1.20), 105 (3.30), 91 (2.23), 79 (0.55), 69 (0.69), 55 (0.52), 43 (0.31), 32 (0.32);  $^1\text{H NMR}$ : 0.927 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 1.253-2.623 (m, 2H,  $\text{CH}_2$ ), 1.253-2.633 (m, 10H, the proton of cyclohexane), 7.372, 7.404, 8.140 (d,  $J = 8.4$  Hz, 8.8 Hz, 8.4 Hz, 2H of each), 8.046-8.066 (m, 6H), 10.114 (s, 1H, CHO).

**4-[4-(4-(4-*n*-Propylcyclohexyl) benzoyloxy)phenyldiazenyl]benzaldehyde (3f)**: Relative molecular mass: 454.56, the mass fraction detected by LC is 98.9 %, orange powder, m.p. 140-141 °C; Anal. Calcd. for  $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3$ : C 76.63, H 6.65, N 6.16; found: C 76.44, H 6.87, N 6.01; IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 2953, 2921 (s, C-H), 2843, 2736 (s, H of aldehyde), 2361, 2343, 1734 (vs, C=O), 1696 (vs, C=O), 1654, 1637 (N=N), 1589, 1559, 1542, 1494 (m, ArH), 1448, 1418, 1376, 1309, 1266, 1223, 1198, 1176, 1137, 1099, 1060, 1010 (vs, C-O-C), 968, 924, 882 (s, *trans*-H-N=N-R), 847, 815 (w, 1, 4-Ar), 761 (w,  $(\text{CH}_2)_n$ ), 727, 698; MS (70 ev)  $m/z$  (%): 454 ( $\text{M}^+$ , 1.48), 440 (0.10), 337 (0.12), 321 (0.02), 307 (0.08), 257 (0.81), 243 (0.20), 229 (100), 227 (2.26), 209 (1.11), 199 (0.03), 187(0.32), 171(0.08), 157(0.17), 145(0.29), 131(1.31), 117 (1.01), 105 (3.52), 91 (2.22), 81 (0.54), 67 (0.66), 55 (0.62), 43 (0.24), 32 (0.23);  $^1\text{H NMR}$ : 0.904 (t, 3H,  $J = 7.5$  Hz,  $\text{CH}_3$ ), 1.120-1.158 (m, 2H,  $\text{CH}_2$ ), 1.304-1.408 (m, 2H,  $\text{CH}_2$ ), 1.433-2.638 (m, 10 H, the proton of cyclohexane), 7.375, 7.445, 8.154 (d,  $J = 8.0$  Hz, 8.0 Hz, 8.0 Hz, 2H of each), 8.137 (b, 6H), 10.104 (s, 1H, CHO).

**4-[4-(4-(4-*n*-Ethylphenyl)benzoyloxy)phenyldiazenyl]benzaldehyde (3g)**: Relative molecular mass: 434.49, mass fraction detected by LC is 98.9 %, orange powder, m.p. 171-172 °C; Anal. Calcd. for  $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_3$ : C 77.40, H 5.10, N 6.45; found C 77.27, H 5.28, N 6.26; IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 2967,

2918, 2874 (s, C-H stretching vibration), 2849, 2734 (s, H of aldehyde), 2361, 2342, 1730 (vs, C=O), 1699 (vs, C=O), 1654, 1637 (N=N), 1598, 1495, 1458 (m, ArH), 1418, 1399, 1280, 1203, 1137, 1081, 1007 (vs, C-O-C), 891 (s, *trans*-H-N=N-R), 830 (w, 1, 4-Ar), 779 (w,  $(\text{CH}_2)_n$ ), 760, 696; MS (70 ev)  $m/z$  (%): 434 ( $\text{M}^+$ , 3.16), 420 (0.22), 406 (0.12), 329 (0.02), 317 (0.11), 300 (0.03), 285 (0.02), 243 (0.14), 226 (0.77), 209 (100), 207 (0.88), 194 (0.10), 181 (3.30), 166 (3.36), 152 (6.83), 141 (0.43), 121 (0.93), 105 (0.70), 93 (1.05), 77 (0.48), 65 (0.68), 57 (0.23), 44 (0.54), 32 (0.40);  $^1\text{H NMR}$ : 1.230 (t, 3H,  $J = 7.6$  Hz,  $\text{CH}_3$ ), 2.659 (q, 2H,  $J = 7.6$  Hz,  $\text{CH}_2$ ), 7.266, 7.372, 7.534, 7.608, 8.208 (d,  $J = 8.0$  Hz, 8.8 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 7.985 (b, 6H), 11.02 (s, 1H, CHO).

**4-[4-(4-(4-*n*-Propylphenyl)benzoyloxy)phenyldiazenyl]benzaldehyde (3h)**: Relative molecular mass: 448.51, mass fraction detected by LC is 98.5 %, orange powder, m.p. 174-175 °C; Anal. Calcd. for  $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_3$ : C 77.66, H 5.39, N 6.25; found C 77.73, H 5.43, N 6.19; IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 2958, 2928 (s, C-H), 2869, 2728, 2676, 2552, 2360, 2341, 1732 (vs, C=O), 1689 (vs, C=O), 1588, 1558, 1507, 1466 (m, ArH), 1428, 1398, 1284, 1206, 1139, 1103, 1006 (vs, C-O-C), 948, 838, 823 (w, 1, 4-Ar), 773, 730 (w,  $(\text{CH}_2)_n$ ), 660, 544; MS (70 ev)  $m/z$  (%): 448 ( $\text{M}^+$ , 5.64), 371 (0.07), 359 (0.06), 344 (0.03), 284 (0.02), 268 (0.04), 259 (0.06), 237 (0.81), 224 (0.35), 211 (0.23), 193 (0.03), 181 (0.19), 164 (0.20), 147 (100), 131 (0.66), 121 (1.30), 119 (3.92), 104 (0.51), 93 (1.64), 91 (7.77), 65 (1.82), 44 (1.37), 32 (0.32),  $^1\text{H NMR}$ : 0.981 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 1.646-1.738 (m, 2H,  $\text{CH}_2$ ), 2.649 (t, 2H,  $J = 7.2$ ,  $\text{CH}_2$ ), 7.293 (d, 6H,  $J = 8.0$  Hz), 7.569, 7.695, 7.932, 8.167, 8.281 (d,  $J = 8.4$  Hz, 8.8 Hz, 8.4 Hz, 8.0 Hz, 8.0 Hz, 2H of each), 10.095 (s, 1H, CHO).

## RESULTS AND DISCUSSION

**Photosensitivity in solution:** The synthesis of all target compounds is outlined in **Scheme-I** and their structural data are shown above. The spectral values are in accordance with the assigned structure. It is known that the azo functional group can do isomerization from the more stable *trans*-isomer to the *cis*-one under illumination of UV-light. The optical absorbance of all target compounds in MeOH solution is summarized in Table-1 and the change of UV-spectrum of representative compound **3a** is shown in Fig. 1. The solutions utilized were kept in the dark for 2 days so that we can infer that the compounds were exclusively in the *trans* form. The UV-spectra were recorded over the same time interval until photostationary states were reached. The maximum time of isomerization were obtained at photostationary states. The spectrum variations are the evidence of the *cis-trans* isomerization of the azo chromophores. Data depicted in Table-1 indicate, before or after irradiation, compounds with same terminal rings have same number and similar position of peaks in UV-spectra. Every peak has a relationship with molecular structure. For example, the sample **3a** in solution with concentration of  $5 \times 10^{-5}$  mol/L (Fig. 1), the small shoulder at ~430 nm is assigned to  $n-\pi^*$  transition and the maximum of the absorbance in the range of 300-380 nm corresponds to a strong  $\pi-\pi^*$  electronic transition of *trans*-isomer of azo-moiety, while the peak at 230 is caused by aromatic ring system. Before irradiation the maximum

absorption wavelength  $\lambda_{\max}$  (nm) of compounds with terminal single six-membered carbon ring are recorded at 228, 334 for compound **3a**, 230, 330 for **3b**, 240, 338 for **3c**, 240, 332 for **3d**, respectively, while after irradiation  $\lambda_{\max}$  (nm) are at 228, 330 for compounds **3a**, 228, 325 for **3b**, 242, 342 for **3c**, 243, 322 for **3d**, respectively. According to these data above, we observed that the UV-light of 365 nm causes the azo bands ( $\pi$ - $\pi^*$  electronic transition) of compounds **3b** and **3d** a little bit more hypsochromic shift than these of compounds **3a** and **3c**, while the other peaks of them caused by aromatic ring system almost stays practically unaltered. Before irradiation the  $\lambda_{\max}$  (nm) of compounds with terminal double six-membered carbon rings are recorded at 242, 332 for compounds **3e**, 241, 334 for **3f**, 331 for **3g**, 327 for **3h**, respectively, while after irradiation,  $\lambda_{\max}$  (nm) are at 245, 329 for compounds **3e**, 245, 328 for **3f**, 294 for **3g**, 293 for **3h**, respectively. We find that UV-light causes the peaks of  $\pi$ - $\pi^*$  transition (the second peak) of the four compounds a hypsochromic shift and the first bands caused by aromatic ring system are not observed in the UV-spectra of compounds **3g** and **3h**. The addition of a carbon in the alkyl chain (from ethyl to propyl) has greater effect on the second peaks of the first four compounds after irradiation. The spectral data before and after irradiation of every compound indicates the terminal alkyl chain has a bigger influence on the azo band than on the aromatic band. It is noteworthy that the terminal propyl chain causes the peak of azo group a bigger hypsochromic shift than terminal ethyl chain of corresponding structure in the first six compounds (Table-2). The electronic effect of alkyl group doesn't present in spectral data of compounds **3g** and **3h**. We observe from the spectral data of compounds **3g** and **3h**, after irradiation, the peaks of  $\pi$ - $\pi^*$  transition of azo group are hyperchromic shifts of 37 nm (from 331 to 294) and 34 nm (from 327 to 293), which are much more than these shifts caused by the first six compounds during the process of *cis-trans* isomerization. This phenomenon suggests that the terminal bi-benzene causes such a great effect on peaks of  $\pi$ - $\pi^*$  transition of azo group in the process of *cis-trans* isomerization that it covers the effect resulted from terminal alkyl group. It means when the number of terminal benzene ring is greater than 1, we can not investigate the effect of terminal alkyl group. The effect of terminal ring system on UV-spectra is deduced from the data of compounds **3a**, **3c**, **3e** and **3g** (with terminal ethyl), **3b**, **3d**, **3f** and **3h** (with terminal propyl). The spectral data of **3a** and **3e**, **3b** and **3d** indicates that the addition of a terminal benzene ring has greater effect on the absorption bands, being more pronounced in the aromatic band than in the azo band, while these of compounds **3c** and **3e**, **3d** and **3f** suggests that the addition of a terminal cyclohexane ring, being more pronounced in the azo band than the aromatic band. In other words, the effect of the addition of a terminal cyclohexane ring presents on the absorption of azo band, while that of the addition of terminal benzene ring works on the absorption of aromatic band. The two terminal benzene rings in compounds **3c** and **3d** cause the first absorption disappeared in the mean time a greater effect presents on the second peak of the azo band after irradiation.

The maximum times of photoisomerization of all these compounds are reached within 70 min for illumination inten-

sities of  $105 \mu\text{W cm}^{-2}$ . The two isosbestic points, located at nearby 295 and 393 nm in Fig. 1, confirm the existence of only two compounds, the *cis*- and *trans*-isomer<sup>14</sup>. Under sunlight, compound **3a** recover its original structure as Fig. 2b shown. Owe to the longer molecular structure, it is difficult for them to convert their shapes from one isomer to another. It almost takes 60-70 min for their complete changing (Table-1). The original absorbance of compound **3a** is  $A_1 = 0.87025$  at 333 nm (Fig. 1a). Subsequent irradiation with sunlight for 70 min causes the absorbance at 334 nm re-increase to  $A_2 = 0.83630$  (Fig. 1b). It is seen that  $A_2/A_1$  is 96 %, *i.e.*, the azo compound isomers do recover 96 %.

**Liquid crystalline properties and photosensitivity in mesophase:** The thermal behaviours of all the target compounds

TABLE-1  
 $\lambda_{\max}$  OF *trans*- AND *cis*-ISOMERS OF  
TARGET MOLECULES IN UV-SPECTRA

Compd.	<i>trans</i> -Isomer $\lambda_{\max}$ (nm)		<i>cis</i> -Isomer $\lambda_{\max}$ (nm)		Time (min) from <i>trans</i> to <i>cis</i> in solution
	I	II	I	II	
<b>3a</b>	228	334	228	330	70
<b>3b</b>	230	333	228	325	60
<b>3c</b>	240	338	242	342	60
<b>3d</b>	240	332	243	322	70
<b>3e</b>	242	332	245	329	60
<b>3f</b>	241	334	245	328	70
<b>3g</b>	–	331	–	294	60
<b>3h</b>	–	327	–	293	70

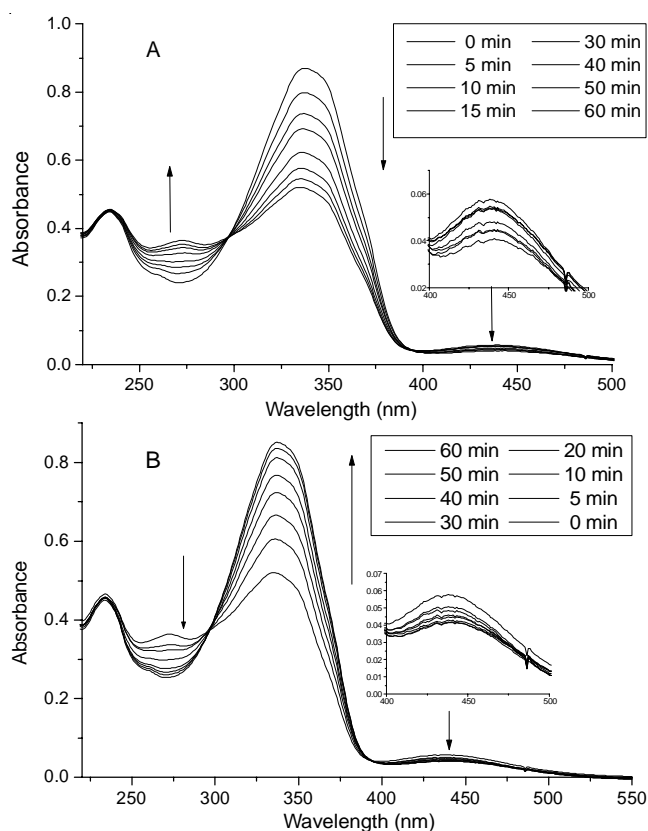


Fig. 1. UV-visible absorption spectrum of compound **3a** in methanol during *trans*-to-*cis* isomerization; (a) under irradiation of UV-light; (b) under irradiation of sunlight). The inset illustrates the small increase of absorption in 430 nm

TABLE-2  
 RESULTS OF DSC MEASUREMENT OF TARGET COMPOUNDS

Compounds	3a	3b	3c	3d	3e	3f	3g	3h
m.p. (°C)	84.6	98.8	132.2	122.5	128.5	140.9	170.1	174.5
$\Delta H$ of m.p. (J/g)	35.56	49.9	52.96	55.25	62.17	42.44	23.17	40.36
c.p. (°C)	190.7	225.6	271.0	267.9	268.9	241.1	275.2	276.5
$\Delta H$ of c.p. (J/g)	1.3320	1.538	1.3597	1.3352	2.777	1.3838	1.890	1.788
Range of mesophase (°C)	106.1	126.8	138.8	145.4	140.4	100.2	105.1	102.0
d.p. (°C)	205.1-388.0	222.4-381.4	287.2-395.0	280.1-404.3	291.8-333.2	290.6-340.1	285.1-392.5	283.1-305.8

\*m.p. is melting point, c.p. is clearing point, d.p. is decomposing point

were investigated by DSC, TGA and POM. The results are summarized in Table-2. The POM micrographs of compounds **3a** and **3b** are shown in Fig. 2. All target compounds exhibit the appearance of textures should belong to nematic phase and their melting point, clear points and decomposing temperature are measured out (Table-2). The temperature ranges of mesophase of these compounds are from 101 to 145 °C. DSC analysis showed a typical nematic phase transition, crystal-to-nematic-to-isotropic. These azo aromatic aldehydes with shorter alkyl chain have wider ranges of mesophase and more thermostable than other polymers of azo group<sup>15</sup>. Among them, compounds **3a** and **3b** with terminal cyclohexane ring have the lowest melting point and clearing point. The m.p., c.p. and range of mesophase of compounds **3c** and **3d** with terminal benzene ring are higher than compounds **3a-3f** had terminal cyclohexane phenyl ring have lower m.p. than compounds **3h** and **3i** had terminal double benzene rings. Among the last four molecules in Table-2, compound **3e** has wider range of mesophase, while the ranges of mesophase of the other three are quite close. Among all the compounds **3d** with propyl and terminal single benzene ring has the widest temperature range of mesophase. In summary, the compounds with terminal benzene ring all have higher c.p. and m.p. than those without terminal benzene structure. In other words, terminal benzene ring in liquid crystalline molecules can increase m.p. in the mean time raise the c.p.

Since the compounds display photosensitivity in solution, it is interesting to check this behavior in their mesophases. Because of the lowest m.p., compound **3a** was chose to check photosensitivity of mesophase. It is well-known that the

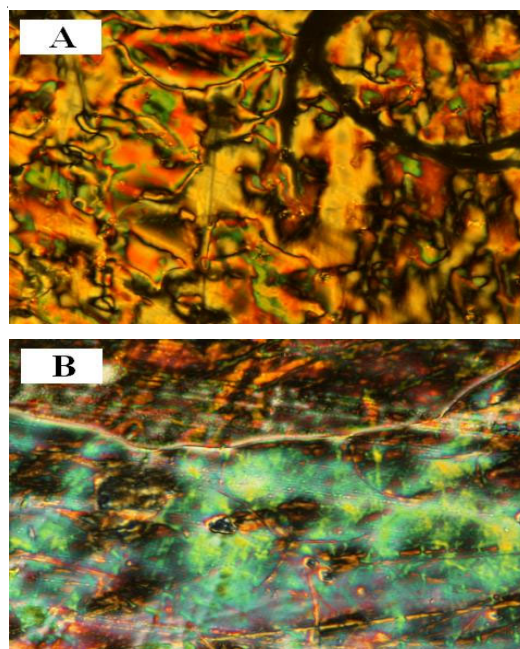


Fig. 2. Textures of some resulting compounds observed under polarizing optic microscope during heating process; (a) the schlieren texture of compound **3a** taken at 110 °C  $\times$  300  $\times$ ; (b) the schlieren texture of compound **3b** taken at 113 °C  $\times$  300  $\times$

molecular shape of *cis*-isomer is so bent that it has no any mesophase observed. After radiating under UV-light of 365 nm each 10 min, the change of texture of compound **3a** was observed by POM (Fig. 3). The textures of compound **3a** observed gradually disappeared as increasing the time of radiation

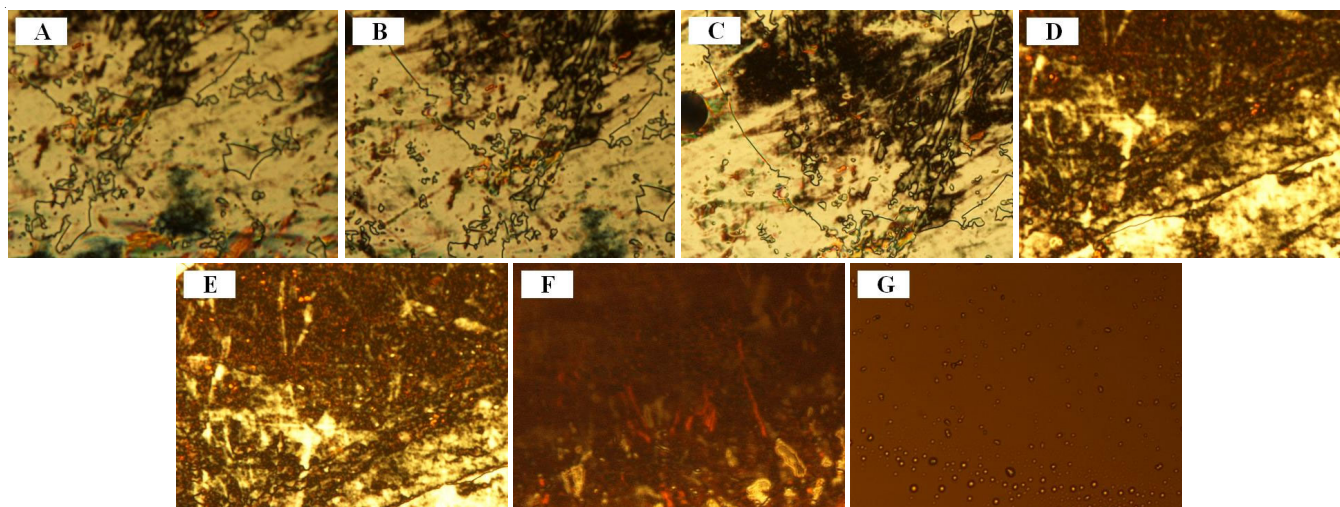


Fig. 3. Texture change during UV-radiation of compounds **3a**; (A) texture after 10 min radiation; (B) texture after 20 min radiation; (C) texture after 30 min radiation; (D) texture after 40 min radiation; (E) texture after 50 min radiation; (F) texture after 60 min radiation; (G) texture after 70 min radiation

of UV-light, indicating the structure of target compound is converted from *trans*-to-*cis*-isomer. The result shows the azo compound can also change their shape from in mesophase.

### Conclusion

Eight new azo aromatic liquid crystal molecules have been prepared by a combination of rigid core involving azo group and different terminal single or double six-membered rings with polar CHO and shorter alkyls chain (C2 or C3) as structural units. The molecular structure allows them to exhibit a phase behavior belong to the nematic, which provides an opportunity to investigate their photosensitivity not only in solution but also in mesophase. All these compounds in a solution of methanol can gradually change their shape under UV-light of 365 nm. Except compounds with terminal bi-benzene structure, terminal propyl group has higher electronic effect on the azo band than terminal ethyl group in UV-spectrum. It is because the electronic effect of terminal bi-benzene structure present to mask that from alkyl group. In other words, the electronic effect of terminal alkyl chain on UV-spectra only presents if there is no or only one terminal benzene rings. The azo compound can recover its *trans*-form at a recovery rate of 96 % under sunlight. We also performed photo-induce studies on mesophase of compounds, which seldom reported until now. Results showed that the molecules can also change their shapes in mesophase under irradiation of UV-light, which are observed by gradually disappearing of mesophasic texture under POM. Although these molecules has shorter alkyl chain, they have so long rigid core that they need long time of radiation of UV-light to change their shape from *trans*- to *cis*-isomers compared to other azo molecules without mesophase<sup>16,17</sup>, further work in this direction is under active investigation.

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21102121) and Natural Science Foundation of Shaanxi Province (No. 2010JM2009).

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